PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference FP19906	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. **PCT/AU2004/000939**	International filing date *(day/month/year)* 12 July 2004	Priority date *(day/month/year)* 18 July 2003
International Patent Classification (IPC) or national classification and IPC **Int. Cl.** [7] C22B 3/00, 3/04, 3/12, 3/44, 19/00, 3/14		
Applicant ZINIFEX LIMITED et al		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 3 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. [X] *(sent to the applicant and to the International Bureau)* a total of **10** sheets, as follows:
      - [ ] sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      - [ ] sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.

   b. [ ] *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or table related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

[X]	Box No. I	Basis of the report
[ ]	Box No. II	Priority
[ ]	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
[ ]	Box No. IV	Lack of unity of invention
[X]	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
[ ]	Box No. VI	Certain documents cited
[ ]	Box No. VII	Certain defects in the international application
[ ]	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of the report
18 February 2005	23 June 2005
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer **B. PREMARATNE** Telephone No. (02) 6283 2407

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/AU2004/000939

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ This report is based on translations from the original language into the following language which is the language of a translation furnished for the purposes of:

☐ international search (under Rules 12.3 and 23.1 (b))

☐ publication of the international application (under Rule 12.4)

☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

☐ the international application as originally filed/furnished

☒ the description:

pages **1, 2, 5-19** as originally filed/furnished
pages***3, 4, 4a** received by this Authority on **18 February 2005** with the letter of **17 February 2005**
pages* received by this Authority on with the letter of

☒ the claims:

pages as originally filed/furnished
pages* as amended (together with any statement) under Article 19
pages***20-26** received by this Authority on **18 February 2005** with the letter of **17 February 2005**
pages* received by this Authority on with the letter of

☒ the drawings:

pages **1/1**as originally filed/furnished
pages* received by this Authority on with the letter of
pages* received by this Authority on with the letter of

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages
☐ the claims, Nos.
☐ the drawings, sheets/figs
☐ the sequence listing (*specify*):
☐ any table(s) related to the sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

☐ the description, pages
☐ the claims, Nos.
☐ the drawings, sheets/figs
☐ the sequence listing (*specify*):
☐ any table(s) related to the sequence listing (*specify*):

* *If item 4 applies, some or all of those sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/AU2004/000939

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 1 - 44	YES
	Claims	NO
Inventive step (IS)	Claims 1 - 44	YES
	Claims	NO
Industrial applicability (IA)	Claims 1 - 44	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)

Claims 1-44 meet the criteria set forth in PCT Articles 33(2)-(4) for novelty, inventive step, and industrial applicability, because the prior art before the priority date of the present claims does not disclose or fairly suggest a process and a plant for upgrading an ore or concentrate that contains metal sulphur minerals and gangue material as disclosed in the present claims. This process and plant have industrial applicability.

provide the more-concentrated source of valuable metal in a substantially non-sulphate form.

SUMMARY OF THE INVENTION

The present invention is based on the realisation that metal sulphur compounds can be dissolved away from their host mineral ore or concentrate by using an ammoniacal solution containing ammonium carbonate (AAC solution) and then selectively precipitated to make a more-concentrated source of metal which is, relatively, sulphur-free.

In a situation in which the mineral ore or concentrate contains a valuable metal such as zinc in the form of sphalerite, the present invention enables the zinc and sulphur constituents to be separated so that the zinc constituent can form a product that is attractive to electrolytic plants.

According to the present invention there is provided a process for upgrading an ore or concentrate that contains metal sulphur minerals and gangue material. The process includes the stages of:

a) selectively leaching the ore or concentrate using an ammoniacal solution containing ammonium carbonate that forms soluble metal ammine complexes;

b) separating the solid and liquid phases formed in stage a) with the liquid phase forming a solution including soluble metal ammine complexes and the solid phase including at least in part the gangue material;

c) removing ammonia and carbon dioxide from the liquid phase formed in step b) under conditions that are selected to facilitate the precipitation of valuable metal(s) and minimise the sulphur content in the valuable metal(s) precipitated; and

d) separating the solid and liquid phases formed in stage c) with the solid phase forming a more-concentrated source of valuable metal.

It will be appreciated by a person skilled in the art of the present invention that stages a) to d), or any of the other stages described above may be carried out consecutively or disjunctively and may, for example, be carried out at different plant sites.

Depending on the operating conditions under which stages a) and c) are carried out, the solids formed may preferentially comprise metal oxides, hydroxides and carbonates.

An advantage provided by the present invention is that valuable metals precipitated in stage c), such as zinc, silver and copper can form a metal salt with an anion other than with a sulphur containing anion such as a sulphate. We have realized that the conditions under which the valuable metal(s) are precipitated impacts on whether the valuable metal(s) can be precipitated as a salt with an anion other than a sulphur containing anion. This has major ramifications because the minimization of sulphur in the precipitate provides significant benefits in downstream processes.

Another advantage is that very few of the major constituents of the gangue material (notably iron and silica) are soluble in an AAC solution and, therefore, will form a major portion of the solid phase formed at stage b).

It is preferred that the AAC solution used in stage a) have a pH ranging from 7 to 10.5.

It is preferred that stage a) be carried out at a temperature ranging from 60 to 99°C when at atmospheric pressure. It is possible that stage a) may be carried out at higher temperatures and pressures.

It is preferred that the method includes adding to stage a) a metal oxidant that undergoes a reduction reaction to facilitate the dissolution of the metal sulphur compounds.

It is preferred that the metal oxidant be in the form of a cupric cation (ie Cu^{2+}). This copper may be all sourced from the ore itself during the leach reaction, or may be supplemented by being added in the form of a copper chemical.

In a situation in which the valuable metal is zinc and the material being upgraded is, for example in the form of sphalerite (ZnS), the dissolution of sphalerite may be represented by the following reaction:

(the next page is Page 5)

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for upgrading an ore or concentrate that contains metal sulphur minerals and gangue material, the process including the stages of:

a) selectively leaching the ore or concentrate using an ammoniacal solution containing ammonium carbonate that forms soluble metal ammine complexes;

b) separating the solid and liquid phases formed in stage a) with the liquid phase forming a solution including soluble metal ammine complexes and the solid phase including at least in part the gangue material;

c) removing ammonia and carbon dioxide from the liquid phase formed in step b) under conditions that are selected to facilitate the precipitation of valuable metal(s) and minimise the sulphur content in the valuable metal(s) precipitated; and

d) separating the solid and liquid phases formed in stage c) with the solid phase forming a more-concentrated source of valuable metal.

2. The process according to claim 1, wherein stage a) is carried out at a pH ranging from 7 to 10.5.

3. The process according to claim 1 or 2, wherein stage a) is carried out at a temperature ranging from 60 to a temperature just below boiling point.

4. The process according to any one of claims 1 to 3, wherein the process includes adding to stage a) a metal oxidant that undergoes a reduction reaction to facilitate the dissolution of the metal sulphur compounds.

5. The process according to claim 4, wherein the metal oxidant can be regenerated by oxidation.

6. The process according to claim 4 or 5, wherein the

metal oxidant is in the form of a cupric cation.

7. The process according to claim 6, wherein the concentration of copper cations supplied to stage a) in the ammoniacal solution is at least 0.15 g/L.

8. The process according to claim 6 or 7, whereby when the metal is zinc and the ore contains sphalerite (ZnS), leaching of sphalerite may be represented by the following reaction:

$$ZnS + 8Cu(NH_3)_4CO_3 + 4H_2O \rightarrow Zn(NH_3)_4CO_3 + 4Cu_2(NH_3)_4CO_3 + (NH_4)_2SO_4 + 3(NH_4)_2CO_3 + 4NH_3.$$

9. The process according to claim 8, wherein the process includes maintaining the concentration of ammonia in stage a) at a level in accordance with the following formulae:

$$[NH_3] \geq ([Zn] + [Cu]) \times 8) + ([SO_4] \times 2)$$

10. The process according to any one of claims 6 to 9, wherein cupric copper is regenerated by oxidation with oxygen according to the following reaction:

$$2Cu_2(NH_3)_4CO_3 + O_2 + 4NH_3 + 2(NH_4)_2CO_3 \rightarrow 4Cu(NH_3)_4CO_3 + 2H_2O$$

11. The process according to any one of claims 1 to 10, wherein an oxygen containing gas is supplied to stage a).

12. The process according to any one of claims 1 to 11, wherein an oxygen-rich gas is supplied to stage a).

13. The process according to any one of claims 1 to 12, wherein stage c) is carried out at a temperature ranging from 90°C to boiling point so as to evaporate

ammonia and thereby facilitate the precipitation of metal compounds.

14. The process according to claim 13, wherein stage c) includes sparging the liquid phase with steam so as to regulate temperature and provide a carrier gas for further ammonia removal.

15. The process according to any one of claims 1 to 14, wherein stage c) is carried out to an end pH of 6.8 or more to minimise the precipitation of metal sulphate minerals.

16. The process according to any one of claims 13 to 15, whereby when the metal is zinc the precipitation of zinc and the evaporation of ammonia occurring in stage c) can be represented by the following reaction:

$$11Zn(NH_3)_4CO_3 + 48H_2O \rightarrow 8Zn(OH)_2.3ZnCO_3.4H_2O\downarrow + 8(NH4)_2CO_3 + 28NH_4OH$$

17. The process according to any one of claims 1 to 16, further including a stage of calcining the solid phase recovered in stage d).

18. The process according to claim 17, wherein the calcination stage is carried out by heating the solid phase formed in stage c) to a temperature ranging from 100°C to 500°C.

19. The process according to any one of claims 1 to 18, wherein the liquid phase recovered from stage d) is treated to precipitate sulphur and compounds containing sulphur from the liquid phase as a salt.

20. The process according to claim 19, wherein a neutralising agent is added to the liquid phase of stage d).

21. The process according to claim 20, wherein the neutralising agent maintains the pH above 7 during the sulphate precipitation stage to minimise the level of ammonia remaining as ammonium hydroxide.

22. The process according to any one of claims 19 to 21, wherein ammonia is removed from the liquid phase recovered from stage d) by heating the liquid phase.

23. A plant for upgrading an ore or concentrate that contains metal(s) sulphur minerals and gangue material, the plant including:

a first stage in which an ammoniacal solution containing ammonium carbonate can selectively leach metal(s) and metal compounds from the ore or concentrate to form soluble metal ammine complexes;

a separator for separating the solid and liquid phases formed, in which, the liquid phase includes soluble metal ammine complexes and the solid phase includes at least in part gangue material;

a second stage that is supplied with the liquid phase formed in the separator and from which ammonia and carbon dioxide are removed under conditions that are selected to facilitate the precipitation of valuable metal(s) and minimize the sulphur content in the valuable metal(s) precipitate; and

a further separator for separating the solid and liquid phases formed in the second stage whereby the solid phase forms a more-concentrate source of valuable metal(s).

24. The plant according to claim 23, wherein the pH in the first vessel ranges from 7 to 10.5.

25. The plant according to claim 23 to 25, wherein the temperature in the first stage ranges from 60 to a temperature just below boiling temperature.

26. The plant according to any one of claims 23 to 25, wherein a metal oxidant is supplied to the first stage which undergoes a reduction reaction to facilitate the dissolution of the metal sulphur compounds.

27. The plant according to claim 26, wherein the metal oxidant can be regenerated by oxidation.

28. The plant according to claim 27, wherein the metal oxidant is in the form of a cupric cation.

29. The plant according to claim 28, wherein the concentration of copper cations supplied to the first stage in the ammoniacal solution is at least 0.15 g/L.

30. The plant according to claim 27 or 28, wherein the metal is zinc and the ore contains sphalerite (ZnS), leaching of sphalerite may be represented by the following reaction:

$$ZnS + 8Cu(NH_3)_4CO_3 + 4H_2O \rightarrow Zn(NH_3)_4CO_3 + 4Cu_2(NH_3)_4CO_3 + (NH_4)_2SO_4 + 3(NH_4)_2CO_3 + 4NH_3.$$

31. The plant according to claim 30, wherein the concentration of ammonia in the first stage is maintained at a level in accordance with the following formulae:

$$[NH_3] \geq ([Zn] + [Cu]) \times 8) + ([SO_4] \times 2)$$

32. The plant according to any one of claims 28 to 31, wherein the metal oxidant is cupric copper, reduced copper is regenerated by oxidation with oxygen according to the following reaction:

$$2Cu_2(NH_3)_4CO_3 + O_2 + 4NH_3 + 2(NH_4)_2CO_3 \rightarrow 4Cu(NH_3)_4CO_3 + 2H_2O$$

33. The plant according to any one of claims 29 to 32, wherein an oxygen containing gas is supplied to the first stage to regenerate the metal oxidant.

34. The plant according to claim 33, wherein the oxygen containing gas is purified oxygen.

35. The plant according to any one of claims 23 to 34, wherein the second stage is carried out at a temperature ranging from 90° to boiling point so as to evaporate ammonia and thereby facilitate the precipitation of metal compounds.

36. The plant according to claim 35, wherein steam is sparged through the liquid phase of the second stage to provide heat and a carrier gas for further ammonia removal.

37. The plant according to any one of claims 23 to 36, wherein the second stage is carried out to an end pH of 6.8 or more to avoid excessive amounts of metal sulphate forming.

38. The plant according to any one of claims 25 to 37, whereby when the metal is zinc the precipitation of zinc and the evaporation of ammonia occurring in stage c) can be represented by a reaction of the form:

$$11Zn(NH_3)_4CO_3 + 48H_2O \rightarrow 8Zn(OH)_2.3ZnCO_3.4H_2O\downarrow + 8(NH4)_2CO_3 + 28NH_4OH$$

39. The plant according to any one of claims 23 to 38, further including a stage of calcining the solid phase recovered in the further separator.

40. The plant according to claim 39, wherein the calcination stage is carried out by heating the solid phase formed in stage c) to a temperature of at least 100°C and preferably, above 300°C.

41. The plant according to any one of claims 23 to 40, wherein the liquid phase from the separator stage d) is treated to precipitate sulphur and compounds containing sulphur from the liquid phase as a salt.

42. The plant according to claim 41, wherein the liquid phase from stage d) be treated by adding a neturalising agent to the liquid phase.

43. The plant according to claim 42, wherein the neutralising agent maintains the pH above 7 during the sulphate precipitation stage to minimise the level of ammonia remaining as ammonium hydroxide.

44. The plant according to any one of claims 41 to 43, wherein ammonia is removed from the liquid phase in stage d) by heating the liquid phase and sparging with steam.